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Production of Poly(carbonate-co-ether) via Catalytic Polymerization of Epoxidized Linseed Oil, Propylene Oxide and Carbon Dioxide

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Abstract. Poly-(carbonate-co-ether) was synthesized via catalytic polymerization between epoxidized linseed oil (ELO), propylene oxide (PO) and carbon dioxide (CO₂) using heterogeneous catalyst namely Co-Zn double metal cyanide (Co-Zn DMC). The influence of polymerization time was studied. It was revealed that the properties of the resultant polymers were affected by the polymerization time. Within the range of polymerization time studied, the maximum average molecular weight (Mn) of the resultant polymer obtained was $6.21 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ with polydispersity index (PDI) of 1.05 at reaction time of 24 hours.

1. Introduction

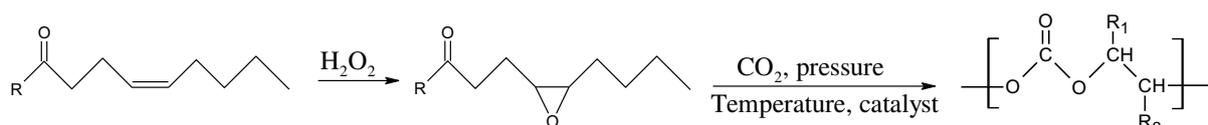
The transformation of carbon dioxide (CO₂) into polycarbonates via copolymerization with epoxides is perceived as an interesting strategy to utilize the abundance of greenhouse gases. After the first breakthrough made by Inoue and coworkers [1] in the year of 1969, copolymerization of CO₂ with epoxides has been studied intensively by researchers whereby diverse kinds of catalysts [2, 3], epoxides [4, 5] and operating conditions [6, 7] have been reported. To date, the most common epoxides used in the copolymerization reaction are propylene oxide (PO), cyclohexene oxide and styrene oxide which all are derived from petroleum feedstocks. However, due to the repeated oil crisis associated with the high price and fear of the exhaustion of the crude oil, more attention was given to the identification of alternative renewable sources, based on natural raw material.

Vegetable oil has become one of the most interesting renewable resources for polymer synthesis because of its universal availability, inherent biodegradability and low toxicity [8-11]. The major components of vegetable oil are triglycerides which comprise of three fatty acid chains combined with glycerol through ester linkage. The length of fatty acid ranges from 8 to 22 carbon, and some of them have chemical functionalities such as hydroxyl groups, epoxide groups, and unsaturation (carbon-carbon double bond) [12]. The naturally occurring functional groups present in triglycerides can be chemically modified prior to polymerization and in some cases use directly to produce vegetable oil-based polymer [13].

Amongst miscellaneous vegetable oils, linseed oil is an excellent option for the synthesis of polymeric materials. This is owing to its chemical structure, which has a large number of



unsaturations with an average of 6.6 double bonds per molecule [14], which could be chemically modified to introduce new functional groups that readily polymerize. For example, the unsaturation present in linseed oil can be chemically modified to introduce functional group like epoxide via epoxidation reactions and subsequently the epoxidized linseed oil (ELO) can be used as a starting material in the copolymerization reaction with CO₂ to produce polycarbonate (Scheme 1).



Scheme 1. Reactions to produce natural polycarbonate from natural fat/fatty acid

This research was undertaken to study the viability of utilizing ELO in the terpolymerization reaction with PO and CO₂ to produce polycarbonate. The effect of reaction time in correlation with the yield and molecular weight of the resultant polymers was also studied

2. Materials and Methods

2.1. Materials

Potassium hexacyanocobaltate (III)(K₃Co(CN)₆), zinc chloride (ZnCl₂), and tertiary butyl alcohol (tert-butanol) were used for catalyst preparation without further purification. For polymerization reaction, ELO used was supplied by Traquisa (Barbera del Valles, Barcelona Spain) whereas PO (>99%) was purchased from Sigma Aldrich. CO₂ of 99.99% purity was used as received. Methanol (CH₃OH) and methylene chloride (CH₂Cl₂) of analytical grade were supplied by Scharlau and Panreac respectively and directly utilized in the experiments.

2.2. Methods

In this work, a typical heterogeneous catalyst used in CO₂-epoxide copolymerization that is Co-Zn double metal cyanide (Co-Zn DMC) is used. The catalyst preparation followed the method as being described by Shaarani et al. [15].

Polymerization took place in a 100 mL stainless steel reactor (Autoclave Engineers, Erie, PA USA) equipped with mechanical stirrer and an automatic temperature controller system. 0.2 g Co-Zn DMC was placed into the dried autoclave together with 10 mL of ELO and 10 mL of PO. The reactor was purged twice with CO₂ and then slowly pressurized to 5.0 MPa. Next, the temperature was raised and maintained at 60°C and the stirring speed was kept constant at 500 rpm to initiate the polymerization reaction. Meanwhile the reaction time was varied between two to 24 hours. Once the reaction ends, the autoclave was cooled down to room temperature, slowly depressurized and opened. A small aliquot of the reaction mixture was removed from the reactor for proton nuclear magnetic resonance (¹H NMR) analysis. The remaining products obtained were purified by dissolving in dichloromethane, precipitated by excess methanol and then dried at room temperature to a constant weight.

Spectroscopic analyses of products were performed using Fourier transform infrared spectroscopy (FT-IR)(Model: Perkin Elmer 1000) and a Bruker NMR spectrometer (Model: Bruker

AMX 300) with ^1H probe and deuterated chloroform (CDCl_3) as the solvent. The number average molecular weight (M_n), the weight average molecular weight (M_w) and polydispersity index (PDI) of the polymer products were estimated using a gel permeation chromatography (GPC) system (Model: Agilent HPLC). Hexafluoroisopropanol was used as an eluent.

3. Results and Discussion

In this study, ELO was used as one of the precursors in the catalytic polymerization reaction with CO_2 . The yield of products and productivity of the catalyst from the terpolymerization reaction between ELO, PO and CO_2 prepared at different reaction time are shown in Table 1. As can be seen from Table 1, no product was collected at reaction time of 2 h which indicates that this polymerization reaction had a long induction period. Nevertheless, as the time rose to 4 h, more meaningful activity was observed. The yield of resultant polymer recorded at 4 h was 1.562 g and increased to 3.720 g at 24 h. Similar trend was observed for the catalytic activity which shown an increment as the reaction time prolonged from 4 h to 24 h. The values of M_n , M_w and PDI estimated from the GPC are also tabulated in Table 1. The results obtained showed that both M_n and M_w of the resultant polymers are affected by the reaction temperature and fall between 5.02×10^5 to $6.21 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ and 5.89×10^5 to $6.54 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$ respectively. Meanwhile, PDI of the resultant polymers showed a little discrepancy between 1.05 to 1.18. The narrow PDI values indicate that the synthesized polymers have a narrow molecular weight distribution (MWD).

Table 1. Effect of polymerization time on terpolymerization of ELO, PO and CO_2

Sample	Reaction Time (h)	Yield ^a (g)	Productivity (g product/ g catalyst)	$M_n/M_w^{b,*}$ $\times 10^5$	PDI ^{b,*}
ELO2	2	/	/	/	/
ELO4	4	1.562	7.81	5.02/5.89	1.17
ELO6	6	1.906	9.53	5.04/5.93	1.18
ELO16	16	2.411	12.06	5.08/5.93	1.17
ELO24	24	3.720	18.60	6.21/6.54	1.05

Reaction conditions: volume of ELO = 10 mL, volume of PO = 10 mL, catalyst loading = 0.2 g, reaction temperature = 60°C , pressure of CO_2 = 5.0 MPa.

^a Weight of the polymer obtained

^b Determined by gel permeation chromatography (GPC)

*Two peaks were observed in the GPC spectrums of the resultant polymers, representing the highest molecular weight of the polymer (quasi-crosslinked sample) also the oligomeric mixtures containing polyether and the unreacted ELO. The molecular weight reported here was from the quasi-crosslinked sample.

The formation of polymeric product was confirmed by both FTIR and ^1H NMR analyses. Fig. 1 displays the FTIR spectrum of product obtained at reaction time of 24 h. As can be seen from Fig. 1, the resultant polymer exhibits a peak at 1740 cm^{-1} which corresponds to the characteristic absorption of the carbonate group ($\text{C}=\text{O}$), confirming the formation of polycarbonate. Nevertheless, in addition to carbonate absorption, a peak at 1231 cm^{-1} confirms the presence of the ether linkage $\nu(\text{C}-\text{O}-\text{C})$, suggesting that the homopolymer part of the epoxide also exists in the synthesized polymer. Besides, the peak which correspond to epoxide group also still visible

indicating not all epoxide was consumed in the polymerization process. In general, the FTIR spectrum of product prepared at polymerization time of 4 h, 6 h and 16 h (Fig. not shown) also demonstrated similar characteristic absorption.

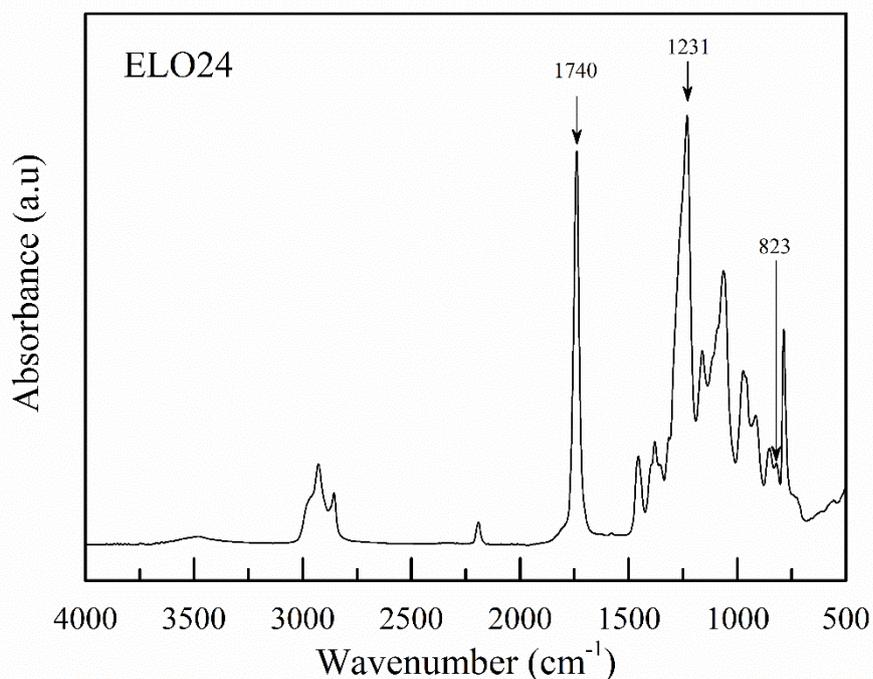


Fig. 1. FTIR spectra of product prepared at reaction time of 24 h (ELO24)

These results were further confirmed by ¹H NMR analysis. Fig. 2 illustrates the comparison of ¹H NMR spectra for ELO monomer and crude ELO24. The appearance of peaks associated to polycarbonate can be seen in the ¹H NMR spectrum alongside with a broad peak at δ 3.5 ppm correspond to ether unit. Also prominent in the ¹H NMR spectrum of the resultant polymer are peaks around δ 2.8–3.2 ppm region associated to epoxy proton signifying that epoxides are not fully reacted in the polymerization reaction most likely due to the steric hindrance owing to the long chain structure of triglyceride. Also notable are the methine proton $-\text{CH}_2-\text{CH}-\text{CH}_2-$ of the glycerol backbone at δ 5.1–5.3 ppm and methylene protons $-\text{CH}_2-\text{CH}-\text{CH}_2-$ of the glycerol backbone at δ 4.1–4.3 ppm which revealed triglyceride structure of ESO is not disturbed [16]. Based on the ¹H NMR spectrum, it can be concluded that the polymer obtain from the terpolymerization of ELO, PO and CO₂ is poly(carbonate co-ether) bonded to the triglyceride chain.

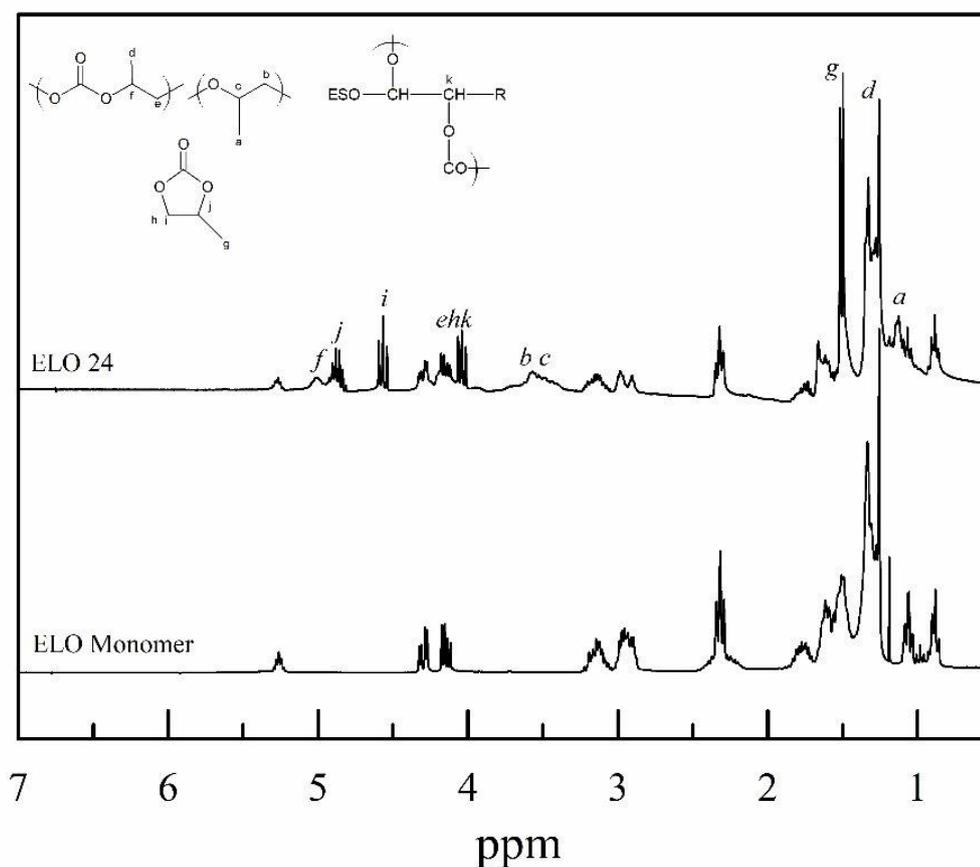


Fig. 2. Comparison of ¹H NMR spectra of ELO monomer and crude ELO24

4. Conclusions

In summary, a bio-based poly(carbonate-co-ether) bonded to the triglyceride chain of ELO has been successfully synthesized via catalytic polymerization of ELO a product from natural resources with PO and CO₂. The presence of each component in the resultant products was verified by means of FTIR and ¹H NMR analyses. The reaction time plays a vital role on the catalyst activity and the properties of the resultant polymers such as yield, Mn, Mw and PDI.

Acknowledgments

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